[SPE]CIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Martensitic Steel Alloys

We, ALLEGHENY LUDLUM STEEL CORPORATION, a corporation organized under the laws of the Commonwealth of Pennsylvania, one of the United States of America, of 2000 Oliver Building, City of Pittsburgh, Zone 22, Commonwealth of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in age hardenable stainless steel alloys and in particular to martensitic stainless steel alloys which may be age hardened to a hardness ranging between 41 R_c and 54 R_c.

Different stainless steels have been recently developed in order to meet the requirements of manufacturers of aircraft and especially aircraft designed for flight at supersonic speeds. These supersonic aircraft are often referred to as "hot" aircraft, since during flight at speeds greater than Mach 1, the surfaces of the aircraft become heated. As a result, particular attention has been given to the material from which such aircraft are manufactured so that the material will exhibit strength characteristics at temperatures of up to 1000° F. In other applications, the temperature range may be extended downwardly to temperatures considerably below −100° F., for example in missiles; thus the effective range of these materials may run the gamut from the so-called cryogenic temperatures to those suitable for the "hot" airplanes. This has led the material suppliers to develop steels and alloys suited to a wide range of useful temperatures. In substantially all of these applications an additional requisite must be present in the material, that being the aspect of exhibiting a good resistance to corrosion. Consequently, interest in stainless steels has increased and the metal manufacturers have developed a family of stainless steels having properties that are intermediate those characterising the conventional stainless steel alloys previously known.

Most of the steels which are presently in use are austenitic stainless steels which, through various forms of subzero cooling and/or double aging, effect an adjustment of the internal chemical composition so that the steel which is normally austenitic at room temperature may be made martensitic in order to obtain the strength advantage of the martensitic structure. In addition, some metal manufacturers have also superimposed an age hardening mechanism in addition to the martensitic mechanism in order to obtain a high degree of strength in the steels. Austenitic metals known to the trade may exhibit an austenitic structure at room temperature which makes the steel amenable to various forms of fabrication, and after fabrication may be heat treated to obtain a variation in the internal chemistry of the steel so that upon cooling to room temperature or to some predetermined subzero temperature, the steel from which the article has been manufactured is transformed to martensite in order to obtain the requisite strength characteristics within the steel. Thereafter the article may be subjected to a low temperature heat treatment to effect a response to tempering and/or aging in order to obtain optimum strength in the material. However, there exists a fundamental difficulty with these so-called austenitic stainless steels in that during severe forming operations, the steel partially transforms to martensite during the forming operation, thus seriously inhibiting the formability of the steel.

Other compositions have also been derived which normally have a duplex microstructure in the annealed condition at room temperature consisting of islands of delta ferrite in a martensitic matrix. This resulted from a particular balance of the chemical components and thus, while these steels exhibit good formability, the strength levels which can be obtained leave a great deal to be desired. In

[*Price 4s. 6d.*]

TABLE II

Chemical Analysis

(% by Wt.)

Heat No.	C	Mn	Si	Cr	Ni	Co	Mo	Ti	Fe
319	0.019	0.010	0.02	15.50	3.37	15.13	2.11	0.50	Bal.
365	0.008	0.006	0.02	15.41	traces	15.86	2.05	0.39	"
367	0.008	0.006	0.02	15.46	3.42	15.39	2.07	0.41	"
368	0.008	0.008	0.02	15.32	3.36	9.99	2.11	0.41	"
369	0.008	0.009	0.02	15.50	3.34	6.99	2.09	0.39	"
370	0.007	0.010	0.01	12.08	3.42	15.19	2.07	0.39	"
371	0.006	0.006	0.02	18.01	3.41	15.48	2.07	0.39	"
373	0.004	0.006	0.01	15.55	6.98	15.53	2.11	0.41	"
452	0.019	0.007	0.02	14.09	3.46	15.50	2.03	0.48	"
454	0.006	0.005	0.02	14.27	3.46	15.57	traces	0.49	"
456	0.005	0.005	0.03	13.04	3.50	15.51	2.94	0.47	"
467	0.005	0.002	0.01	12.04	3.46	15.86	4.12	0.47	"

As stated hereinbefore, the alloying elements which are utilized in the composition of the steel alloy of the present invention must be maintained within the range set forth hereinbefore in Table I. The effect of the elements cobalt, nickel, chromium and molybdenum on the hardness of the steel of the invention is set forth in Table III:

strip having a thickness of 0.230". As hot rolled, samples were cut for hardness and tensile testing and thereafter the hot rolled band was annealed, pickled and cold rolled to 0.129" in thickness. Hardness tests on the samples cut from the hot rolled band which were annealed at 1600° F. for 25 minutes and air cooled revealed a hardness of 30 R_c. Specimens from the hot rolled strip after annealing at 1600° F. for 25 minutes and air cooling, were subjected to a tensile test and the test results indicated a .02% yield strength of 51.6 ksi, a .2% yield strength of 94.4 ksi and a tensile strength of 142 ksi. The elongation measured over the 2-inch gauge length was 15.5%. Other specimens from the hot rolled band after annealing were subjected to a subzero cooling to −100° F. for 16 hours followed by air warming and thereafter these specimens were aged at 950° F. for four hours and air cooled. As thus treated, these specimens had a hardness of 45.6 R_c, indicating an increase in hardness of 15.6 R_c units. Tensile tests conducted on the aged alloy indicated a .02% yield strength of 183.9 ksi, a .2% yield strength of 212.5 ksi, a tensile strength of 219.9 ksi and an elongation, as measured over a 2-inch gauge length, of 14%. Thus it is clear that the commercial heat exhibited an outstanding response to provide an age hardened martensitic stainless steel alloy having superior mechanical properties.

Additional annealed specimens from the hot rolled band were subjected to a cold working operation and were cold reduced 45% without difficulty. Thereafter the specimens were subzero cooled to −100° F. for a period of 16 hours, air warmed, aged at 950° F. for four hours and thereafter air cooled. As this cold worked and heat treated, the steel alloy exhibited a hardness of 50.8 R_c, thus exhibiting a further increase in the hardness. Tensile tests revealed a .02% yield strength of 249.1 ksi, a .2% yield strength of 263 ksi, an ultimate strength of 266 ksi and a per cent elongation as measured over the 2-inch gauge length of 4.0%. Again, the specimens exhibited a high degree of necking during the tensile test. Thus from the foregoing it is clear that the commercial heats of this material exhibit an outstanding combination of mechanical properties, as substantiated by the test data set forth hereinbefore.

It has also been noted that the steel alloy of the present invention exhibits an outstanding degree of formability. Bend tests on sheet material have been made and the steel alloy in the annealed condition was bent 180° over a pin having a diameter which measured twice the thickness of the sheet. No cracking was noted in said bend test. In addition, circular blanks measuring 4—11/16" in diameter were cut from said commercial heat No. 23932 and were thereafter drawn into cups without any adverse effects being noted. These cups measured 2—11/16" in diameter, thus illustrating a 42.7% reduction. This excellent reduction, coupled with the fact that the steel alloy of the present invention in its fully martensitic condition has an extremely low rate of work hardening, as witnessed by the fact that the alloy can be cold worked to accomplish greater than a 50% reduction of cross sectional area of the strip without any adverse effects taking place, is a clear indication that the alloy of the present invention has an outstanding degree of formability for a martensitic steel. Yet, through the proper heat treatment the alloy of the present invention may be heat treated to develop an outstanding combination of mechanical properties.

The steel alloy of the present invention, because of low carbon content, has an excellent degree of corrosion resistance to the various media and more importantly, if the alloy is balanced so that the cobalt content is near the lower limit of 3% and the nickel content is increased to near its upper limit of 7%, the alloy, while not attaining the high level of mechanical properties, will none the less possess an excellent degree of resistance to stress corrosion. This is a very important factor in some applications where some of the strength characteristics can be sacrificed in order to take advantage of the stress corrosion properties of the steel. As amply illustrated by the test data contained in the foregoing specification, the steel alloy has an outstanding degree of ductility and possesses an extremely attractive ratio of notch tensile strength to ultimate tensile strength, thus making the alloy of the present invention particularly applicable for use in aircraft designed for flights at supersonic speeds.

The steel alloy can be readily welded, and, since it is a martensitic steel alloy, the application of a simple aging heat treatment is effective for imparting a high level of mechanical properties thereto without the decrease of warpage through a high temperature heat treatment.

WHAT WE CLAIM IS:—

1. An age hardenable martensitic stainless steel alloy containing from traces to 0.5% carbon, from traces to 0.25% of each of manganese, and silicon, from 10% to 18% chromium, from 0.1% to 7% nickel, from 3% to 16% cobalt, from 0.1% to 8% molybdenum, from 0.1% to 1.3% titanium, and from 0% to 0.1% of each of calcium, boron and zirconium, the balance being iron with incidental impurities.

2. The age hardenable martensitic stainless steel alloy of Claim 1 wherein the maximum amount of carbon is 0.03%, the maximum amount of manganese is 0.15%, the maximum amount of silicon is 0.15%, the amount of chromium is between 12 and 15%, the amount of nickel is between 2 and 7%, the minimum amount of cobalt is 10%, the amount of

molybdenum is between 1 and 6%, and the maximum amount of titanium is 1.0%.

3. The age hardenable martensitic stainless steel alloy of Claim 1 wherein there is a balance between the ferrite forming elements and the austenite forming elements to bring the composition within the area AcBCDaA of the accompanying drawing, the steel exhibiting a martensitic structure having a maximum hardness in the annealed condition, prior to aging, of 35 R_c.

4. The age hardenable martensitic stainless steel alloy of Claim 3 wherein there is a balance between the ferrite forming elements and the austenite forming elements to bring the composition within the area AcbaA of the accompanying drawing.

5. The martensitic stainless steel alloy of Claim 1 obtained by aging the steel, after transforming it to martensite, at a minimum temperature of 600° F., preferably between 900 and 1050° F., for a period of time of at least four hours, the said steel exhibiting a minimum hardness after such treatment of 45 R_c.

6. The martensitic stainless steel alloy of Claim 1 which has been subjected to cold working to effect a reduction in the cross-sectional area of between 25 and 50% followed by cooling to a temperature of no lower than −100° F. and thereafter aging at the temperature range between 900—1050° F., the said steel exhibiting a minimum hardness of 45 R_c after such treatment.

7. An article of manufacture formed from the martensitic stainless steel alloy defined in any one of Claims 1 to 6.

8. A process of making the martensitic stainless steel alloy defined in Claim 4 comprising subjecting a composition falling within the area AcbaA of the accompanying drawing to an anneal at a temperature of from 1500 to 2100° F., and preferably of from 1550 to 1700° F., followed by cooling to a temperature not lower than −100° F. and thereafter aging the alloy at a temperature of from 600° F. to 1100° F., and preferably between 900 and 1050° F., for a period of at least four hours.

9. A process of making the martensitic stainless steel alloy defined in any of Claims 1 to 3 comprising subjecting a composition falling within the area BCDabcB of the accompanying drawing to an anneal at a temperature of from 1500 to 2100° F., and preferably of from 1550 to 1700° F., followed by cold working of the steel to effect a reduction in the cross-sectional area of between 25 and 50%.

10. A process of making the martensitic stainless steel alloy defined in any one of Claims 1 to 4 comprising subjecting a composition falling within the area AcBCDaA of the accompanying drawing to an anneal at a temperature of from 1500 to 2100° F., and preferably of from 1550 to 1700° F., followed by cold working of the alloy and cooling the alloy to a temperature not below −100° F., and thereupon aging the alloy at a temperature of from 600 to 1100° F. and preferably of from 900 to 1050° F.

11. An age hardenable martensitic stainless steel alloy according to Claim 1 and being composed as described herein with reference to the accompanying drawing.

12. A process of making a martensitic stainless steel alloy of the composition defined in any one of Claims 1 to 6, the said process being substantially as described herein with reference to the accompanying drawing.

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